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[10] This loop occurs because the trial wave function is assumed to be translationally invariant and would not appear if a more general trial function were used. See Ref. 2.

New Method to Measure Structural Disorder: Application to GeO_2 Glass*

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A new method is presented for measuring thermal or structural disorder. The additional disorder in the first Ge-O and Ge-Ge distances in amorphous GeO_2 was measured by comparison with crystalline (α-quartz) GeO_2, and showed no additional disorder in the Ge-O distances but deviations in the Ge-Ge distance consistent with a ±6.5° variation about a Ge-O-Ge bond angle of 130°. These results rule out the proposed microcrystalline models.

This Letter introduces a new method to determine the disorder in noncrystalline or crystalline matter. The method follows from an advance in interpreting the extended x-ray-absorption fine-structure (EXAFS) data. The technique is able to measure accurately substantially smaller amounts of disorder than more conventional techniques such as x-ray or neutron scattering. To illustrate the possibilities, GeO_2 glass is studied and the disorder in the first two shells around Ge atoms is determined for the first time as are their average position and the coordination of the first shell. By comparing the disorder in the glass to corresponding values in the crystalline homomorph, it is proved that the microcrystalline model cannot describe the glassy structure.

Previously we have shown[1-3] that Fourier transforms of EXAFS can be interpreted in terms of the local atomic structure about the kind of atom whose edge is being studied. This paper extends the analysis to the measurement of amorphous systems.

Consider the real part of the Fourier transform of EXAFS of both crystalline GeO_2 (α-quartz structure) and amorphous GeO_2 as shown in Fig. 1. The data were taken from the Ge K-edge EXAFS at $T = 77°K$ so that the curves represent the location of atoms about an average Ge atom in the material. The data were normalized so that both curves are on the same (per atom) scale and

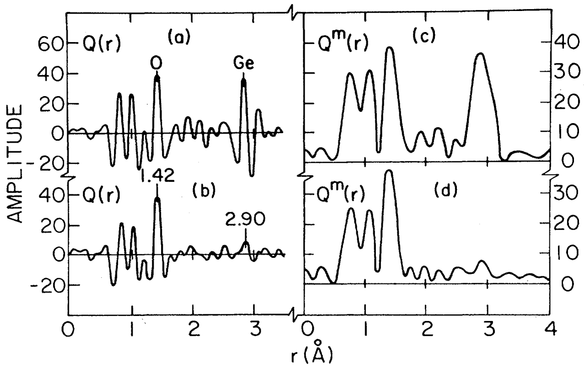

FIG. 1. (a),(b) The real part Q and (c),(d) the magnitude Q^m of the Fourier transform of the Ge edge EXAFS in (a),(c) crystalline (α-quartz) and (b),(d) amorphous GeO_2. The data are normalized to the same scale and transformed over the same interval in k space (2.2–17.5 Å^{-1}).

the transforms were taken over the same region in k space. These data have been presented previously[4] along with a description of the experiment and samples. The α-quartz structure is used for comparison since its EXAFS spectra has been shown previously to be similar to the amorphous spectrum.[4,5] What is important to note for this paper is that the structure up to 1.5 Å (which has been identified as arising from the four O atoms which are bonded to each Ge atom) is essentially identical in both curves in both location and magnitude. The location of the atoms are shifted from their position in real space by an understood phase shift.[6] The big tailing of structure from the O peak towards the origin is not completely understood, but does not interfere with determination of the disorder. The structure around 2.9 Å is due to the next-nearest atom (Ge) and is located at the same position in both curves although its amplitude in the amorphous curve is only $\frac{1}{5}$ of the amplitude in the crystalline material.

A quantitative measure of the disorder can be obtained by determining from the data the Debye-Waller–type factor introduced by disorder[7,8] which multiplies the contribution of the jth shell by $\exp(-2\sigma_j^2k^2)$, where k is the wave vector of the ejected photoelectron and σ_j^2 is the mean-square displacement of the relative distance between the absorbing atom and the atoms in the jth shell.

The use of a Debye-Waller–type factor assumes that the atoms in a shell are distributed about the average position $\boldsymbol{R}_j$ with a Gaussian probability proportional to $\exp[-(r-R_j)^2/2\sigma_j^2]$, where σ_j is much smaller than the interatomic spacing. As shown later it is found that σ_j is small in this sense for the first two shells, the only discernable ones. A determination whether the displacements are Gaussian or not can be obtained from the experimental data as discussed in relation to Eq. (1) below.

The greater sensitivity of EXAFS to disorder compared to more conventional techniques arises because EXAFS retains phase information which, in the Fourier transform, produces a structure for each shell in real space of positive and negative variations that occur over a distance of about 0.1 Å (see Fig. 1) so that any disorder of the order of 0.1 Å drastically reduces the amplitude of the structure. For those shells which are similar in the number, position, and kinds of atoms and differ only by disorder we have shown[6] that

$$\ln[\chi_j(\mathrm{G})/\chi_j(\mathrm{C})] = -2[\sigma_j^2(\mathrm{G}) - \sigma_j^2(\mathrm{C})]k^2, \qquad (1)$$

where k and σ have been defined above and G and C stand for glass and crystalline, respectively. χ_j is the EXAFS for the jth shell and is found by isolating the contribution from the jth shell in Fig. 1 and retransforming only that portion back to k space. A plot of the ratio from the left-hand side of Eq. (1) versus k^2 should give a straight line whose slope gives a measure of the difference in disorder between the glass and crystalline materials. If the displacements of the atoms in the jth shell about the average position R_j are not Gaussian, then the left-hand side of (1) will not vary simply as k^2 but will have a different k dependence. Thus, such a plot is an experimental check on the validity of the assumed Gaussian variation.

In Fig. 2 these plots are shown for the first shell of $\mathrm{GeO_2}$. In the first shell the straight line gives $\sigma_1^2(\mathrm{G}) - \sigma_1^2(\mathrm{C}) = 0.0000 \pm 0.0003$ with an intercept of 0.0 ± 0.02. This intercept equals $\ln[N_1(\mathrm{G})/N_1(\mathrm{C})]$, where N_1 is the number of atoms in the first shell of either the G or C form, and is an independent confirmation that each material has the same coordination number within an uncertainty of 2%. Only six points are plotted because these represent the number of statistically independent points which may be plotted over the range of the data because of the finite range in r space which was taken to find χ_1. The zero slope verifies quantitatively that the disorder of the tetrahedron of the oxygen first neighbors about the Ge atoms is very small in the glassy state.

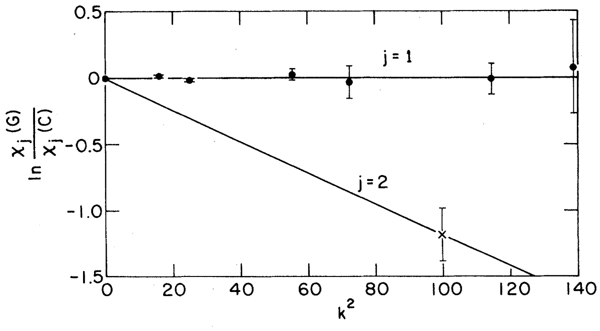

FIG. 2. A plot of $\ln[\chi_j(\mathrm{G})/\chi_j(\mathrm{C})]$ versus k^2 for the first ($j=1$) and second ($j=2$) shells in $\mathrm{GeO_2}$ as determined from Fig. 1. The first shell was determined from Fig. 1 over the range 0.2–2.2 Å and the second shell was taken from 2.4–3.4 Å.

For the second shell a similar analysis would not be as convincing. The signal-to-noise ratio in the amorphous state was too small and only a few points could be plotted since the region used to define the second shell in r space was much smaller. However, with these reservations, the data of the second shell are consistent with a Gaussian displacement though we cannot rule out other distributions which deviate somewhat from the Gaussian form. Instead, if it was assumed that the number of atoms in the amorphous peak is the same as in the crystalline peak, which is consistent with x-ray radial-distribution data,[9] then the point (0, 0) could be used as one of the data points in the plot. The straight-line plot of (1) is then most accurately defined by the point $k=10$ where the signal-to-noise ratio was the greatest. This straight line gives a value $\Delta\sigma_2 = 0.077 \pm 0.014$ Å, where

$$\Delta\sigma_2 = [\sigma_2{}^2(G) - \sigma_2{}^2(C)]^{1/2}. \qquad (2)$$

Since the amplitudes of the crystalline and amorphous peaks both occur at the same distance this result means that the amorphous Ge-Ge distances vary because of a ±6.5° variation about the crystalline Ge-O-Ge bond angle of 130°. Our results are summarized in Table I. The fixed Ge-O bond length of 1.74 Å and the Ge-O-Ge bond angle of 130° ± 6.5° which has been measured by EXAFS can now be compared with earlier x-ray and neutron measurements[9-11] and proposed models[12-16] for this structure.

The similarity of the Ge-O and Ge-Ge distances between the crystalline and amorphous GeO_2 is consistent with the earlier x-ray measurements. However none of these measurements could estimate the disorder about the average distance since it was much smaller than the experimental resolution. The structural models which have been proposed to explain these data include both random-network models[12,13] and microcrystalline models.[14-16] In the random-network models the structure is built up from GeO_2 tetrahedra which are connected by the bridging oxygen except that there are deviations about bond angles such that long-range periodicity is destroyed. The most quantitative model for a glass has been given by Bell and Dean[12] but for SiO_2 instead of GeO_2. They propose a deviation (full width at half-maximum) of 24° about an average angle of 153°. Converting our mean deviation to full width at half-maximum would give only a 16° spread in angle. Some of this discrepancy may arise because the Bell and Dean model was fit to amorphous SiO_2 which has a larger Si-O-Si bond angle (144°) than the corresponding angle in GeO_2. Mozzi and Warren[17] in a very careful x-ray-scattering measurement and model calculation of SiO_2 found an average bond angle of 144° with a full width at half-maximum of 37°, so that there is a larger bond-angle distribution in SiO_2 than in GeO_2.

The other structural model is the microcrystalline model of Karle and Konnert[14-16] proposed on the basis of long-range fluctuations in their measured radial-distribution functions after the effects of the first three peaks were removed. They have concluded that GeO_2 is mostly composed of 15–20-Å-sized crystallites of tridymitelike regions. This is not consistent with our data. Although all of the tetrahedral polymorphs of GeO_2 have the same first Ge-Ge distance, so that it is not possible to distinguish different structures on the basis of second-peak position, crystalline regions of the extent predicted by Konnert and Karle[14-16] would not give the distribution in bond angles measured by our technique.

The signal-to-noise ratio in our χ_2, the inverse transform of the Ge shell back to k space, is such that we can estimate that the fraction of the sample that remains crystalline in the glass [i.e., does not have the k dependence of (1)] is 0.0 with an rms uncertainty of 0.1. Taking the limit of

TABLE I. Parameters for GeO_2 glass. r_1 and r_2 are the distances between Ge and first-neighbor O and Ge, respectively; $\Delta\sigma_1$ and $\Delta\sigma_2$ are the increased amount of disorder in the corresponding r. N_1 is the number of oxygen first neighbors. The distances are all given in angstroms.

	r_1	$\Delta\sigma_1$	N_1	r_2	$\Delta\sigma_2$	$\theta_{\text{Ge-Ge}}$ (deg)
Glass	1.74	0.00 ±0.018	4.0 ±0.08	3.15	0.077 ±0.014	130 ±6.5
Crystalline (hexagonal)	1.74	···	4	3.15	···	130

uncertainty that 10% of the sample could remain crystalline and noting that the microcrystalline regions are surrounded by other microcrystalline regions of different orientation, we can estimate the size of such regions. Assume that the microcrystalline grain boundary region is about 4 Å thick and the measured disorder in the Ge peak comes from such regions. Then we estimate that each microcrystalline region is about 3.8 Å in radius, only 1.8 Å of which is undistorted. The undistorted region is smaller than the unit cell of the tridymite structure proposed by the microcrystalline model[14-16] and thus is not feasible.

It is important to note that the determination of disorder in EXAFS is more direct and accurate than for more conventional methods where model calculations are required. This is because in EXAFS crystalline solids are handled on exactly the same footing as noncrystalline solids, allowing a direct comparison between the noncrystalline solid and its crystalline homomorph, canceling out all unknowns.

In conventional diffraction methods, crystalline solids have an inherently different diffracted line shape than noncrystalline solids. The sharp diffracted line shape of crystalline solids is qualitatively changed to one of finite width in the cold-worked, small-crystalline and amorphous forms,[18] while the disorder produced by thermal vibrations maintains the sharp peak, only decreasing its weight. In EXAFS all of these cases are qualitatively on exactly the same footing, giving the powerful option of directly comparing with the crystalline form. It is this characteristic that distinguishes EXAFS as such a potentially powerful tool to determine accurately short-range disorder.

In summarizing, using an advance in analyzing EXAFS we have quantitatively determined for the first time the mean square of the increased disorder in the first- and second-shell distances about Ge in the glassy state of GeO_2 as summarized in the table. The coordination number around Ge in the glass remains 4 oxygen to within our accuracy of 2%. These results definitely rule out the microcrystalline model for GeO_2 and, although no proposed random-network model quantitatively fits our data, there is no reason to believe that such a model can not be devised.

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